Joint institute for nuclear research

A COMPREHENSIVE STUDY OF RUINED MURAL FRAGMENTS FROM THE 12th CENTURY CHURCH OF TRANSFIGURATION OF OUR SAVIOR ON THE NEREDITSA HILL (VELIKY NOVGOROD, RUSSIA)

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The Church of Transfiguration of Our Savior on the Nereditsa Hill

- ✓ UNESCO World Heritage Site;
- ✓ The first mention is in the Novgorod first Chronicle;
- ✓ Built in 1198 (6706);
- ✓ Painted in 1199;
- ✓ The chronicle indicates the name of the architect of the church: "… and master was Korov Yakovich from Lubyanaya street".

Research objectives:

- Identification of wall painting pigments;
- Determination of the elemental composition of plasters;
- Comparison of two 12th century monuments using statistical methods.

Researches

Paint layers

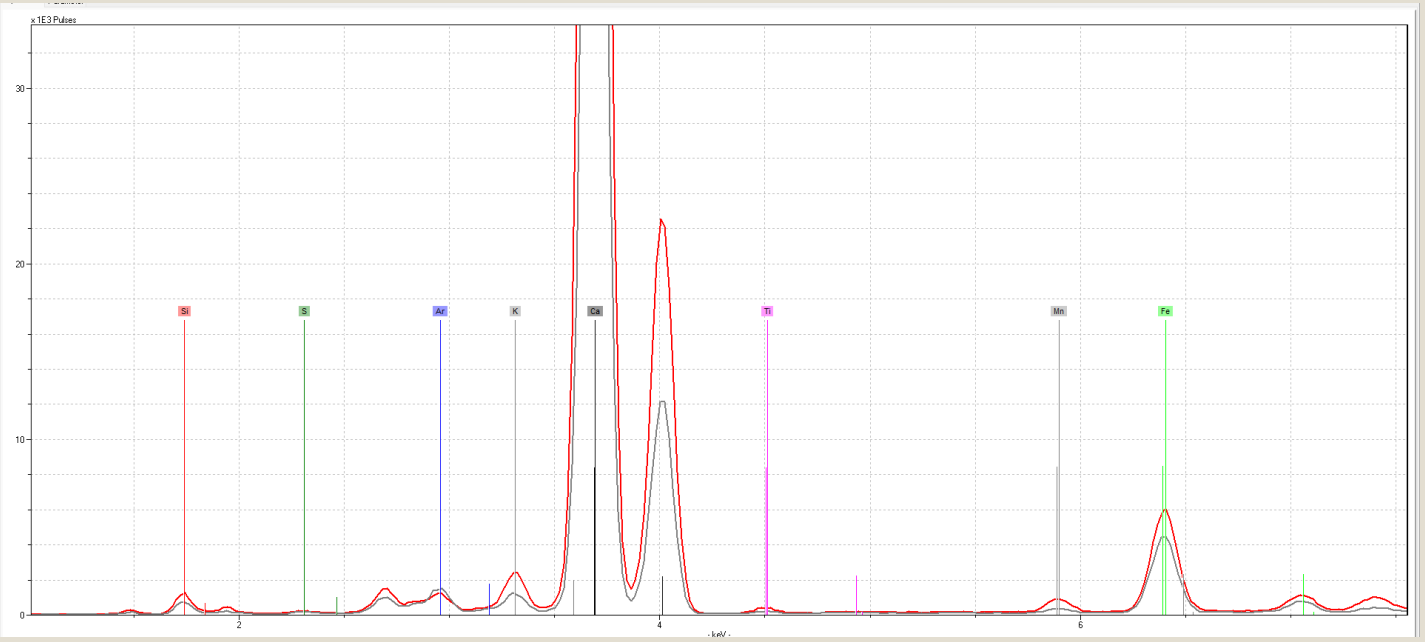
- X-ray fluorescence analysis (XRF)
- Raman spectroscopy
- Polarized microscopy
- Stratigraphy
- Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS)

Plasters

- Neutron activation analysis (NAA)
- Statistical analysis of NAA data
  - Hierarchical cluster analysis
  - Principal component analysis
  - K-means method

X-ray fluorescence analysis (XRF)

- Each fragment was researched from the side of the paint layer and from the side of the plaster; spectrum plasters used it as a background;
- The program Artax was used to process the spectra;
- The assumption of pigmented composition based on XRF was made.

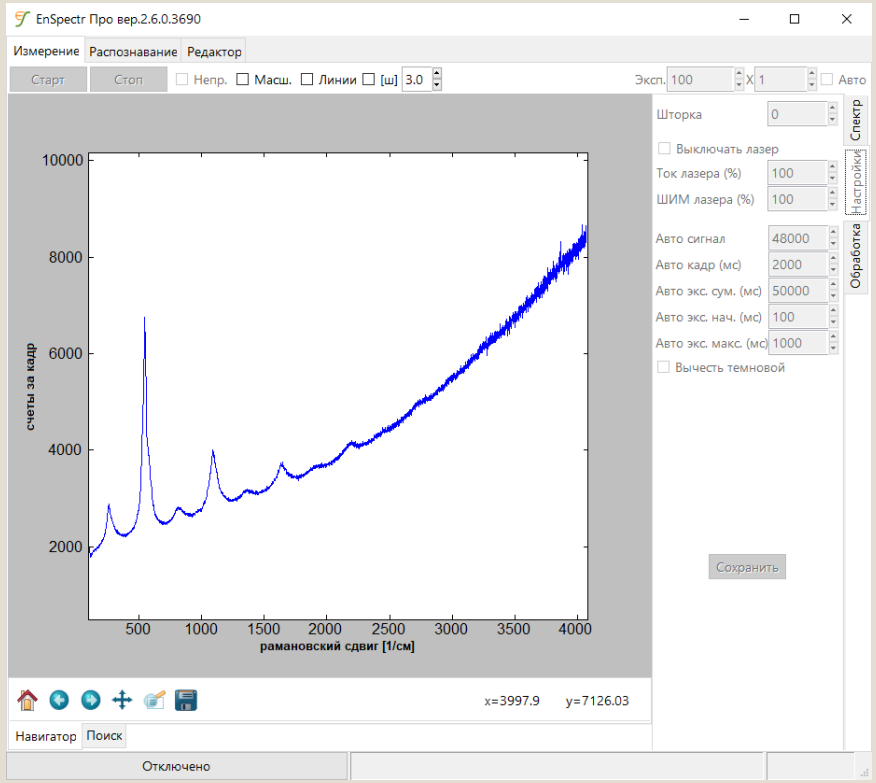


Portable Analyzer Tracer 5i (Bruker)

Micro-Raman spectroscopy

Raman microscope
M532/785/1064 (En-spectr)

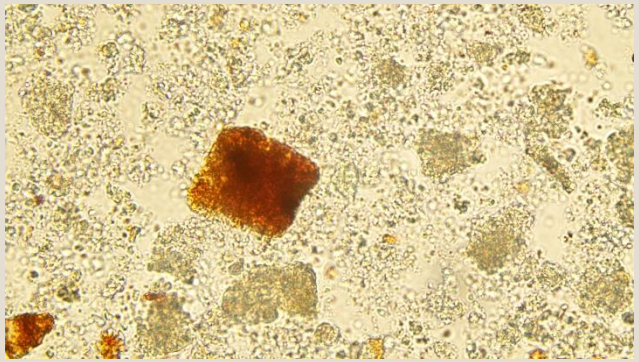
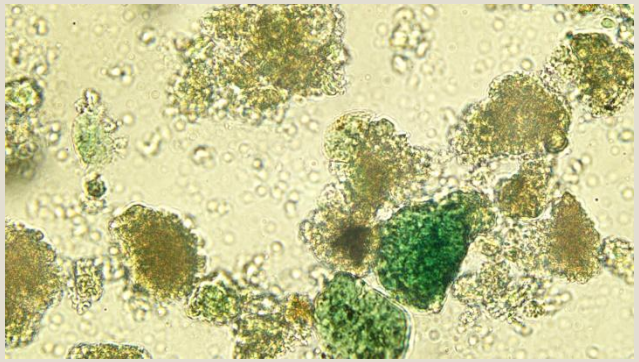
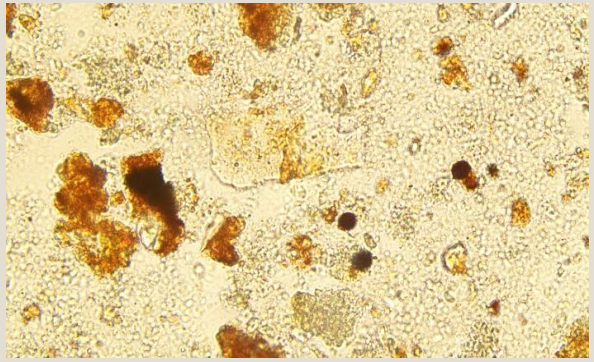
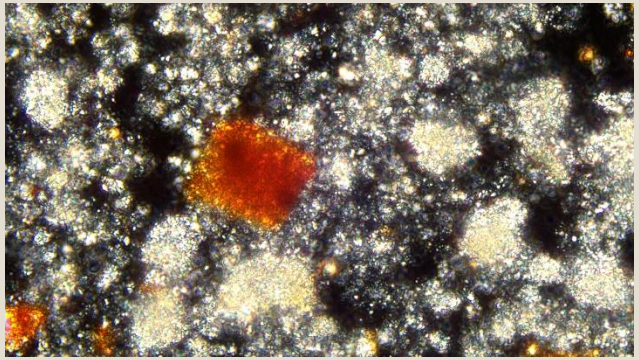
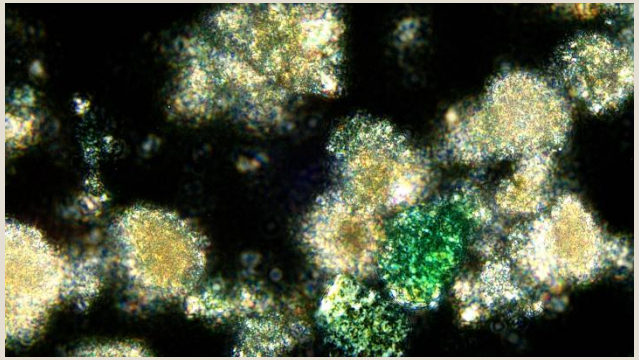
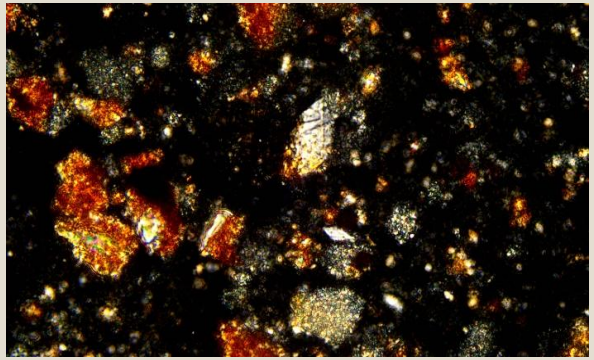
- Confirmation of the pigment composition of fragments;
- Possibility of obtaining spectra of individual paint layers and individual particles of mixed pigments;
- Processing spectra was carried out in the program EN-spectr.



Program En-spectr

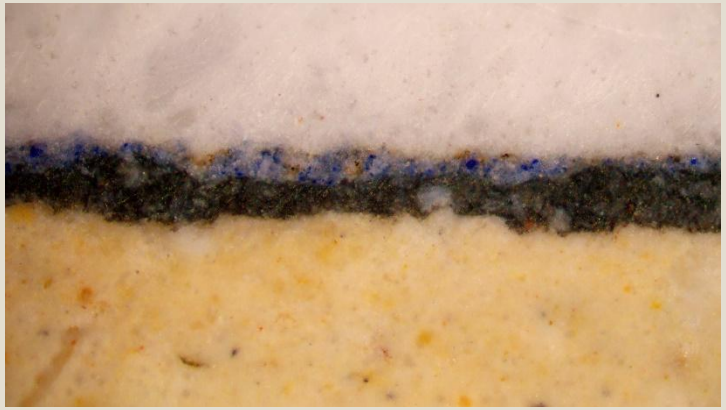
Polarized microscopy

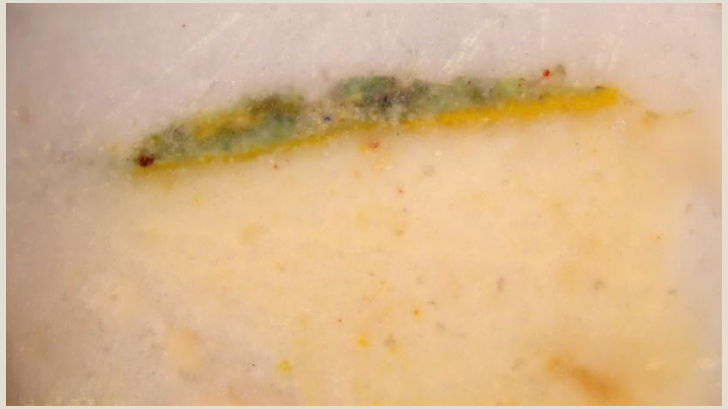
To prepare slides for polarized microscopy particles of the paint layer were placed in Canadian balsam and covered with a cover glass.

Stratigraphy

- Samples were placed in Sorel cement for preparation of cross-sections. For the preparation of cement $MgCl_2$ with MgO were mixed;
- The samples were placed in the prepared paste perpendicular to glass plane;
- After the cement solidified the samples were polished until all layers were appearance completely.





Fragments with red paint layer

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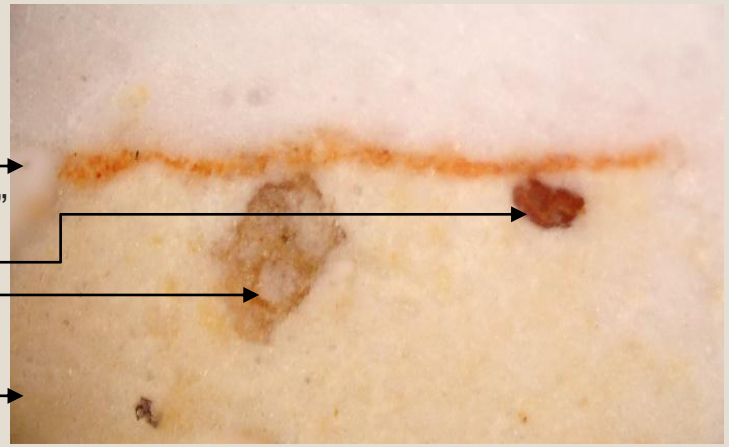
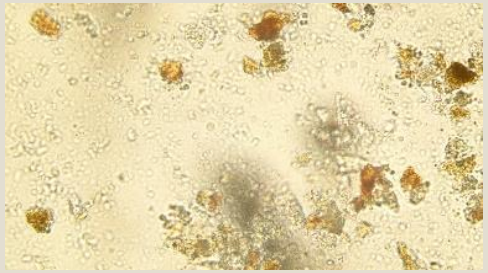
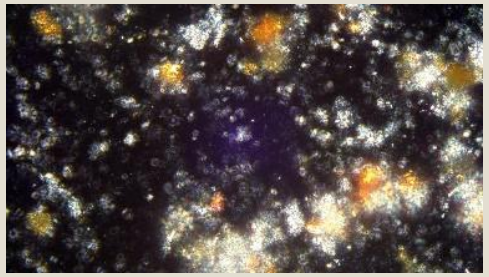
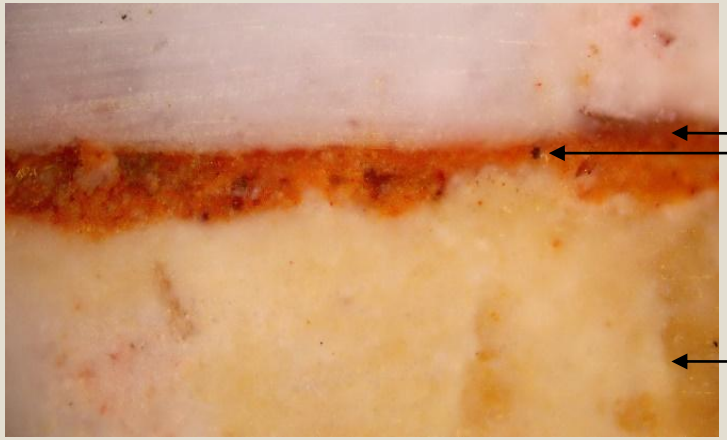
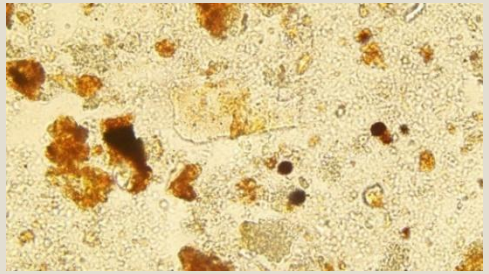


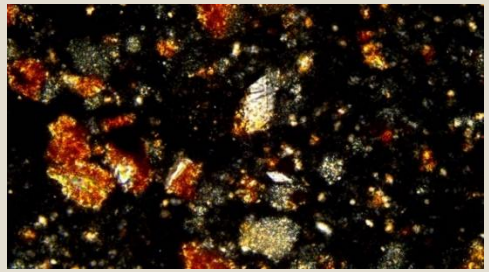




8/171







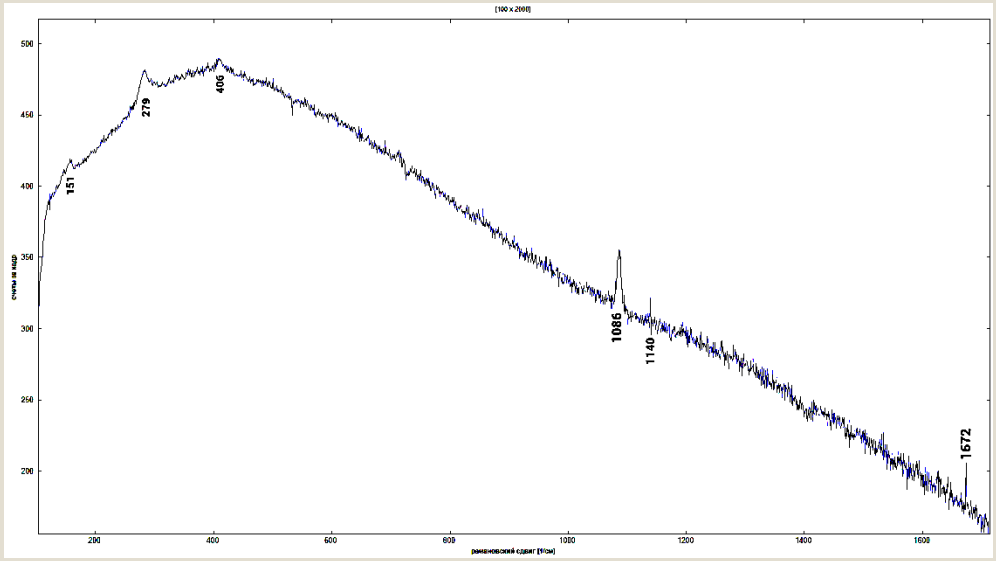
Fragments with red paint layer

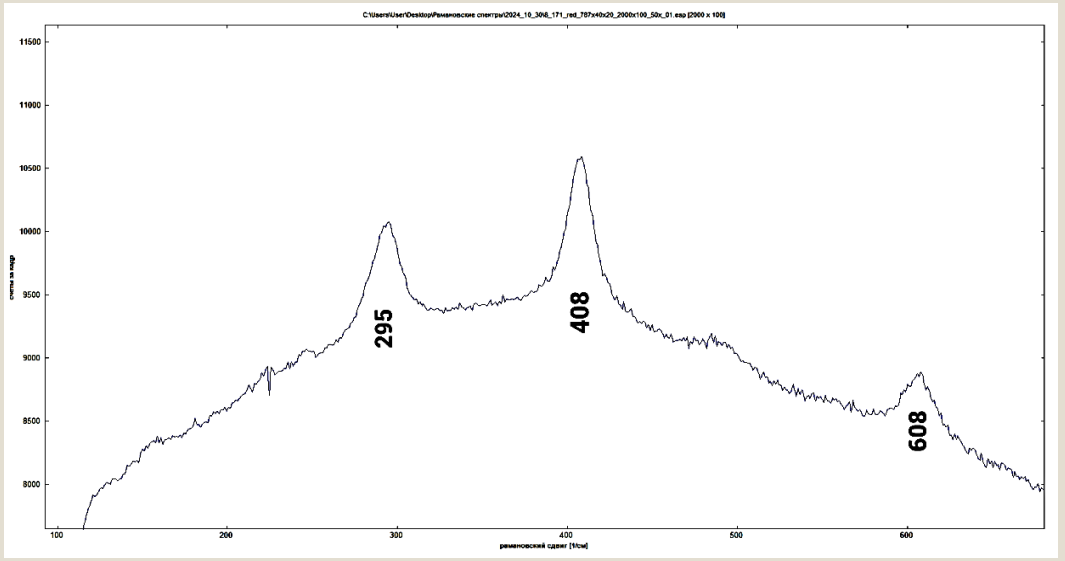
XRF

Color (8/167)	Chemical elements
Orange	Ca, K, Si, Fe, Al, S, Ti, Mn, P, *Zn, V, Cr*

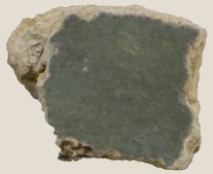
Color (8/171)	Chemical elements
Red	Ca, K, Si, Fe, Al, Mn, Ti, P, *V, Zn, Mg*

μ-Raman





Fragments with green paint layer



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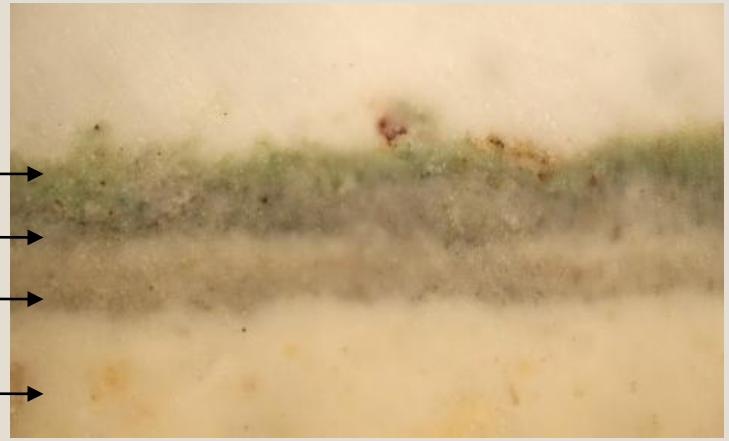

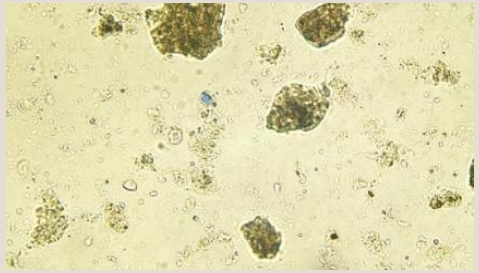

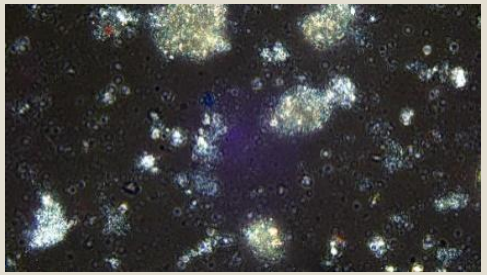

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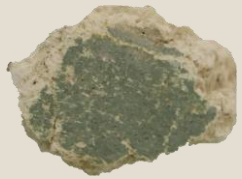
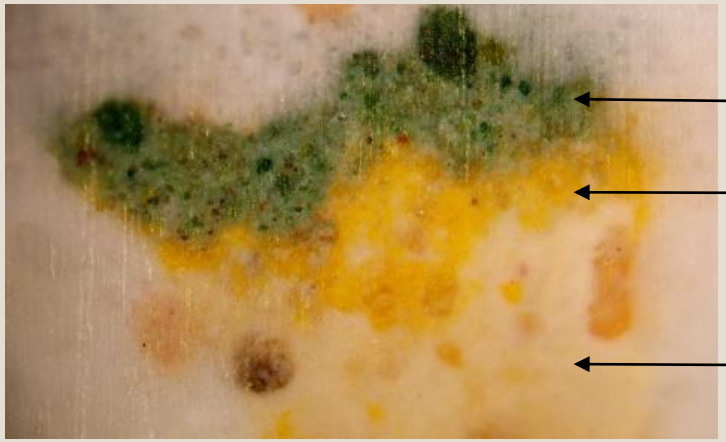
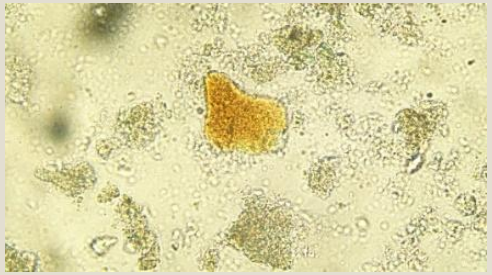
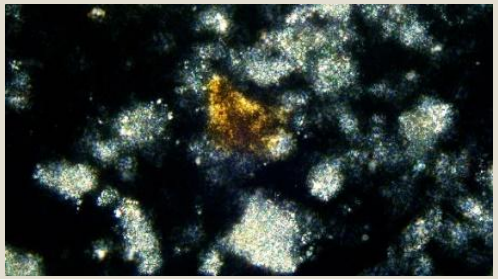








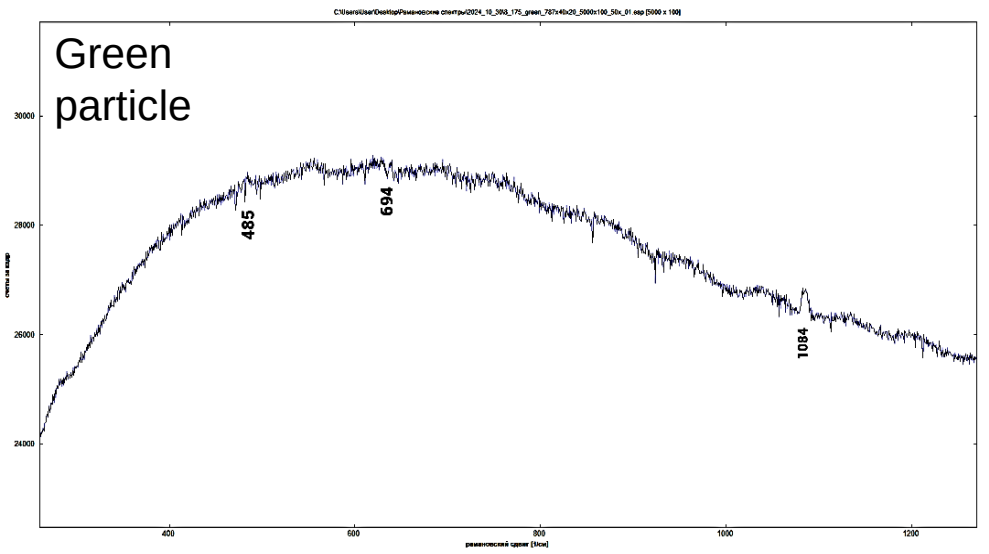
Fragments with green paint layer

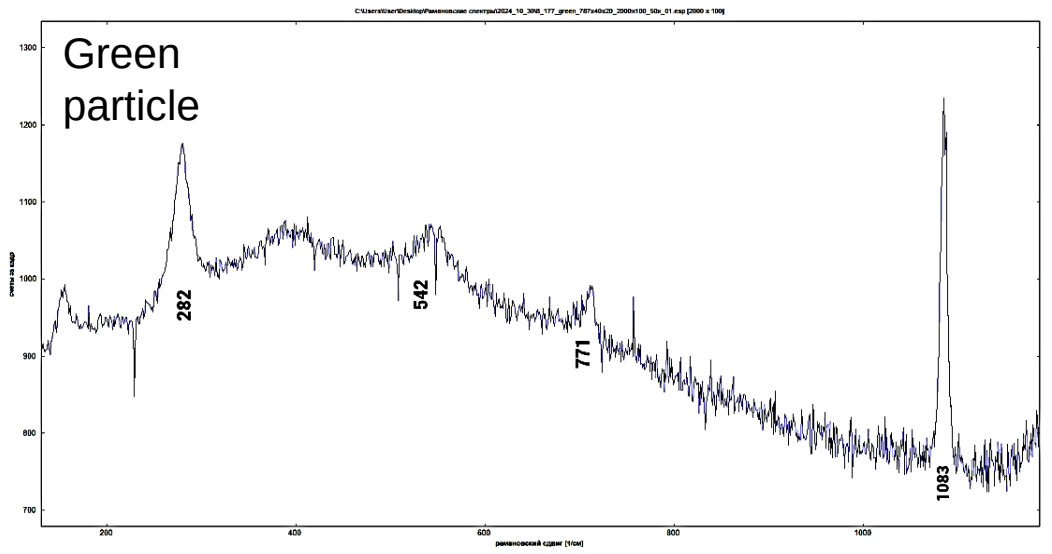
XRF

Color (8/175)	Chemical elements
Green, grey	Ca, K, Si, Fe, Al, Mn, Ti, S, Cr, P, *V, Zn, Cu*

Color (8/177)	Chemical elements
Green, yellow	Ca, K, Si, Fe, Al, Mn, Ti, S

μ-Raman





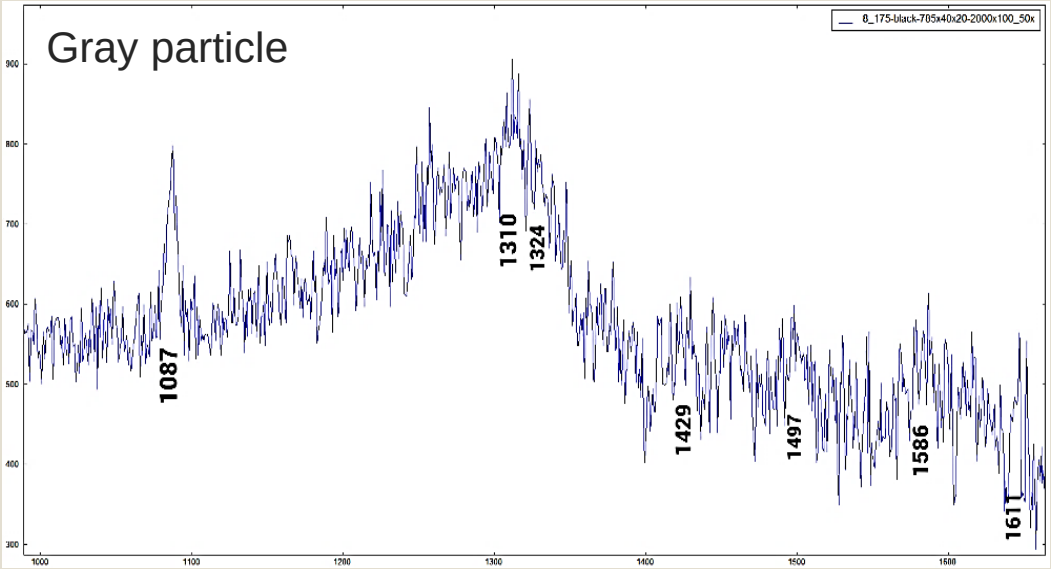
Fragments with green color layer

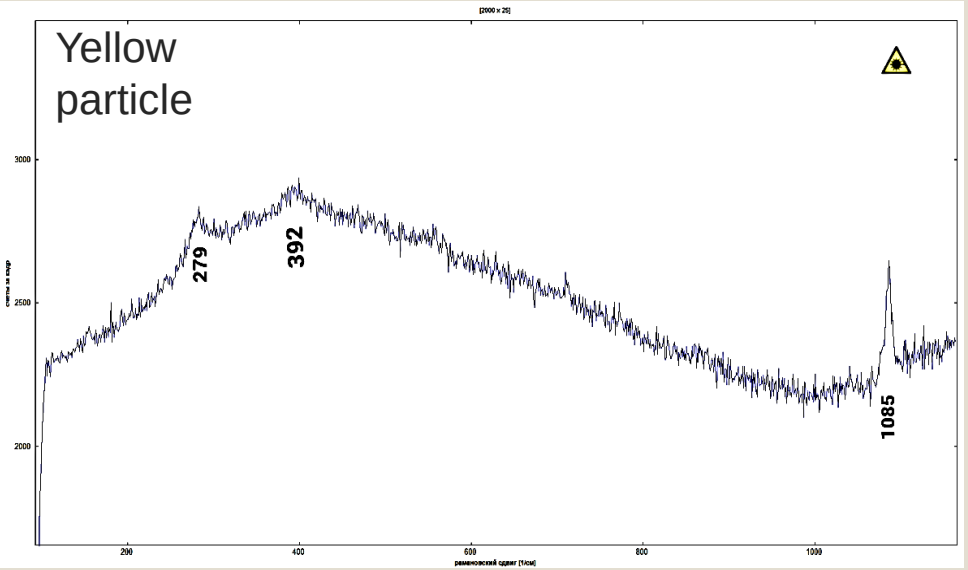
XRF

Color (8/175)	Chemical elements
Green, gray	Ca, K, Si, Fe, Al, Mn, Ti, S, Cr, P, *V, Zn, Cu*

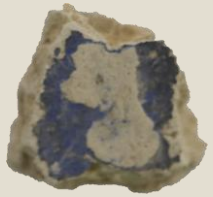
Color (8/177)	Chemical elements
Green, yellow	Ca, K, Si, Fe, Al, Mn, Ti, S

μ-Raman





Fragment with blue paint layer



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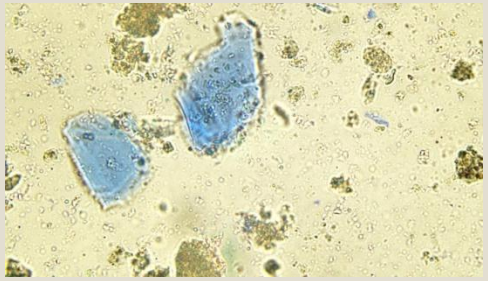
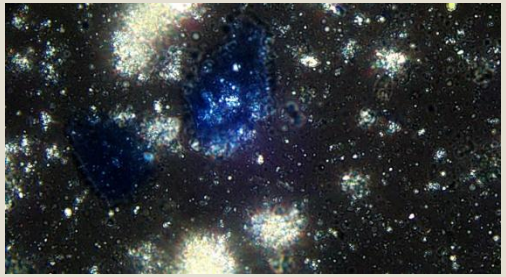
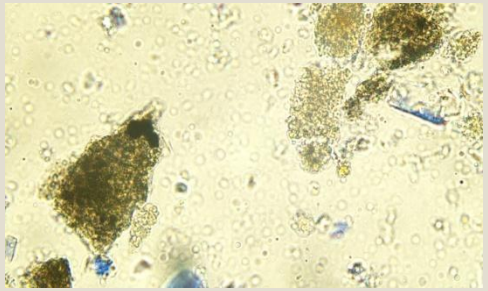
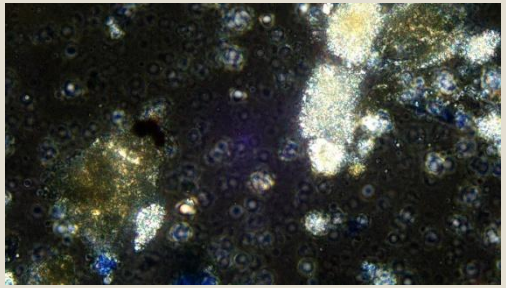
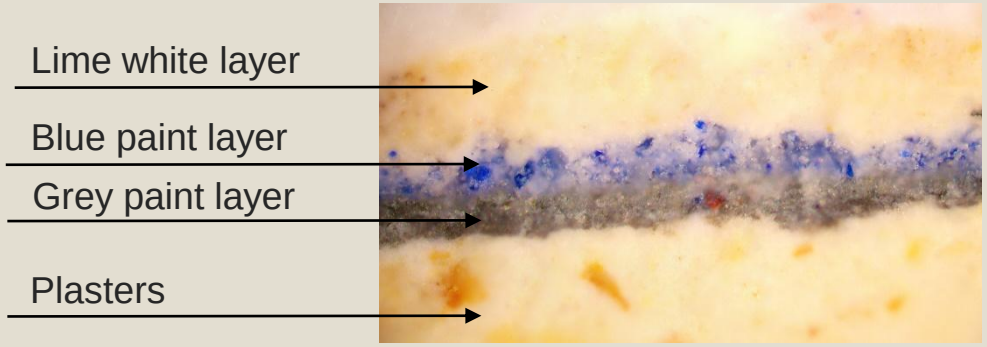
Intended pigments:

- Lazurite
- Smalt (?)
- Soot

Micrographs

Sample cross-section

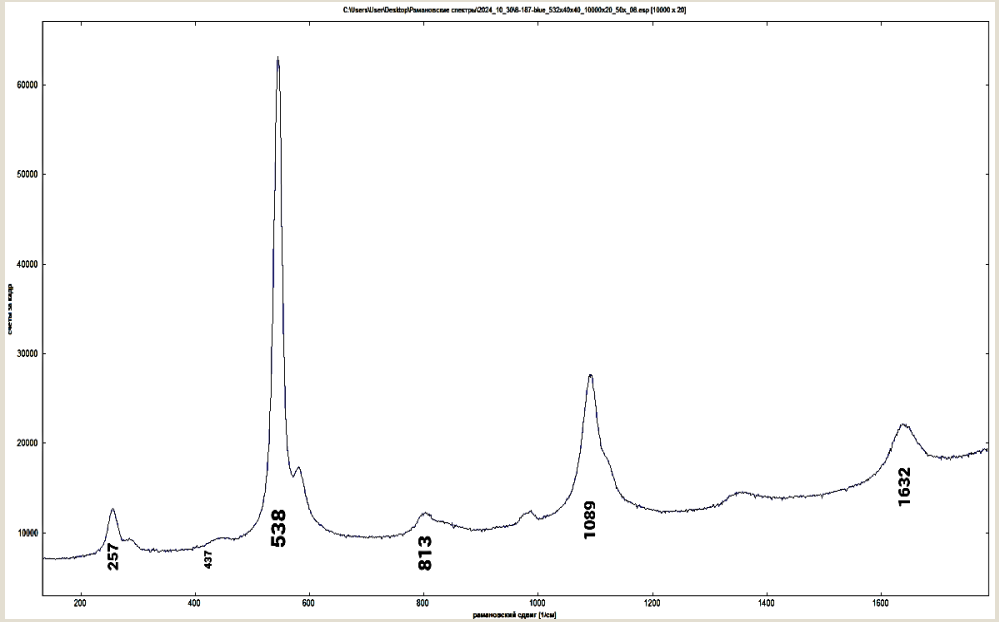


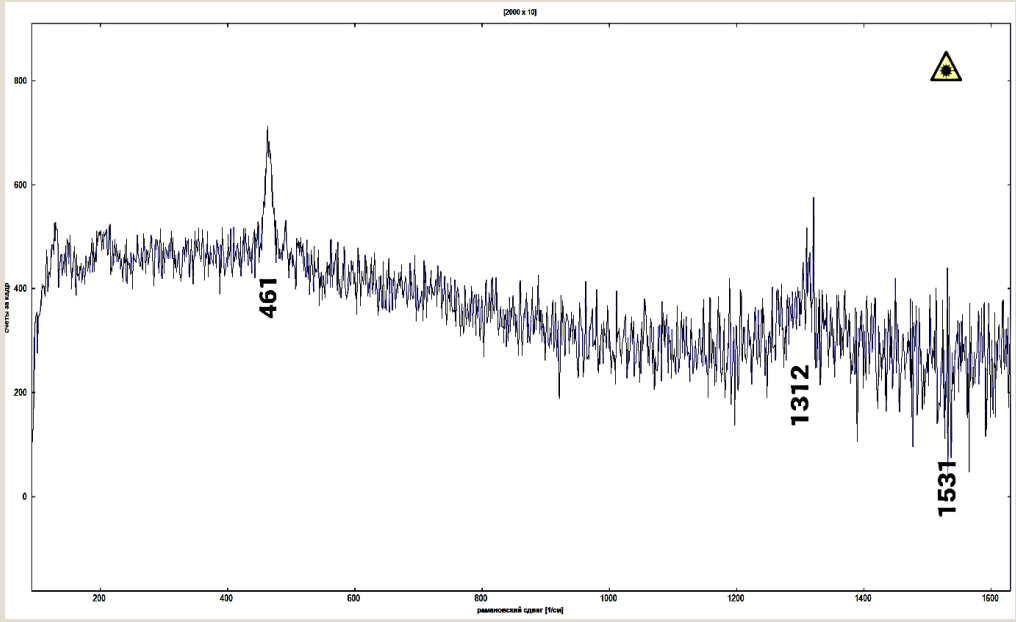
Fragment with blue paint layer

XRF

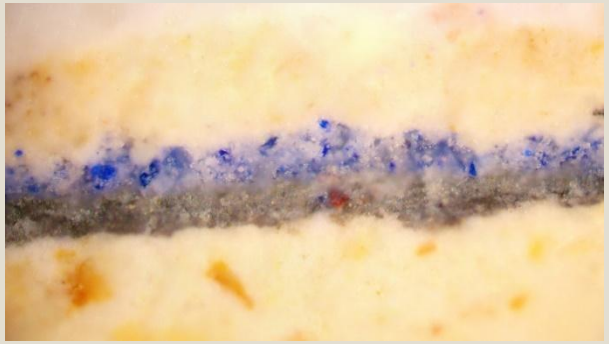
Color (8/187)	Chemical elements
Blue, Grey	Ca, K, Si, Fe, Al, Mn, Ti, S

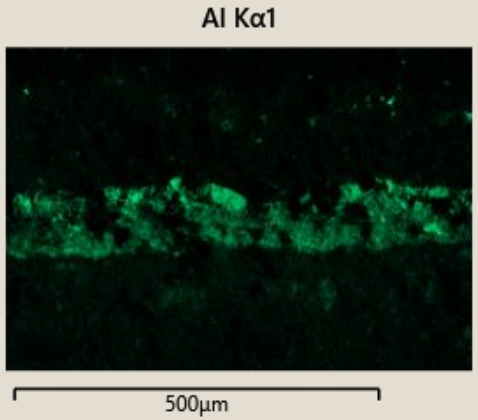
μ-Raman

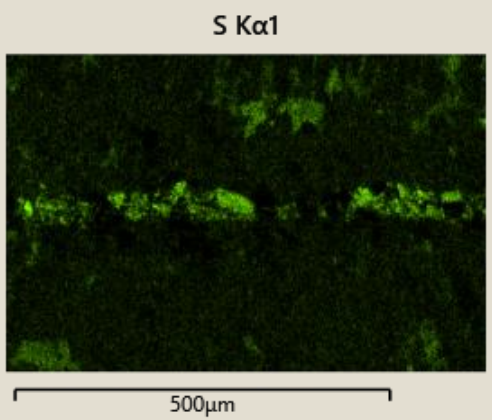


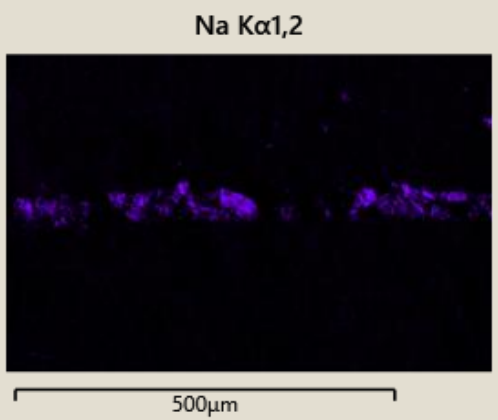


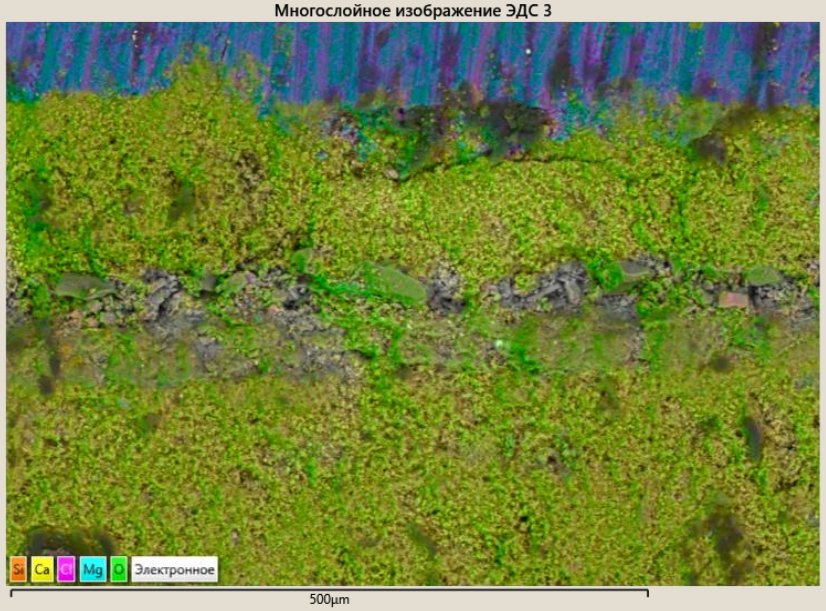
Fragment with blue paint layer

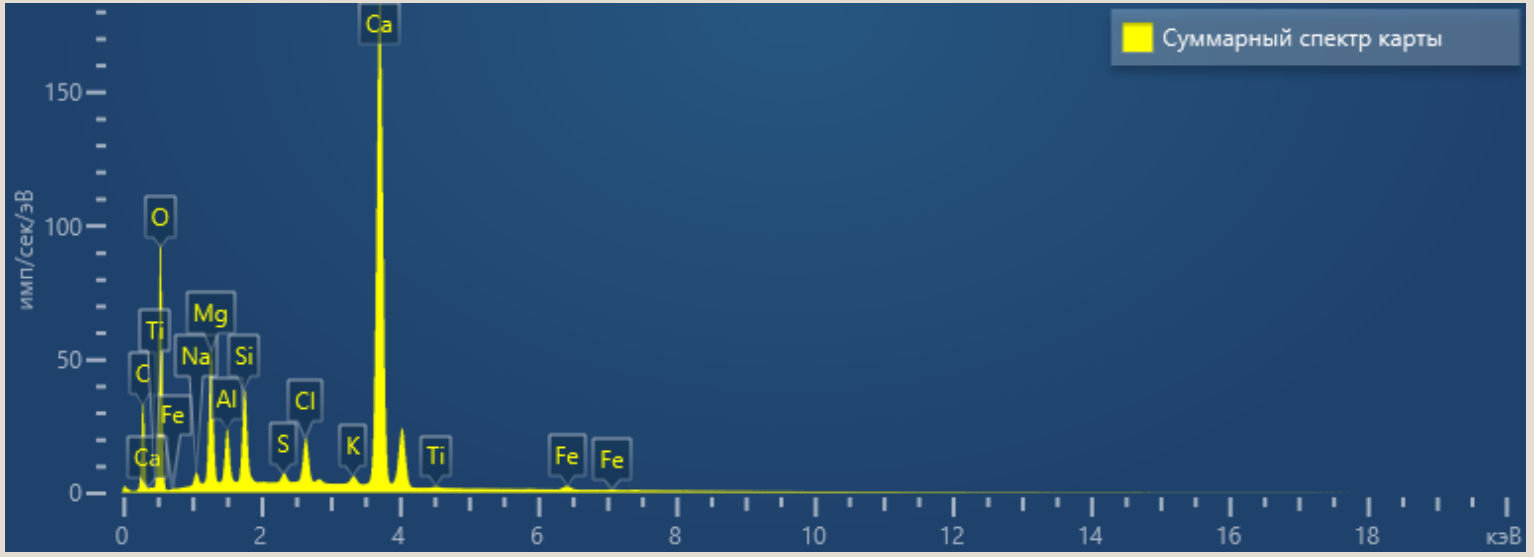












Emission spectrometer EDS Fullframe SEM IQSCAN

Fragment with yellow paint layer

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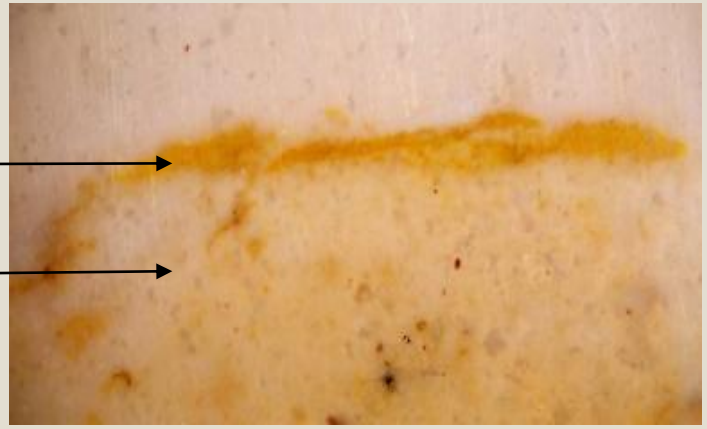
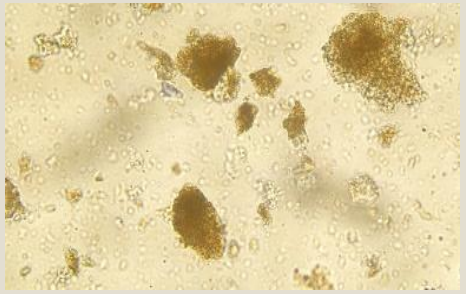
Suggested pigment:

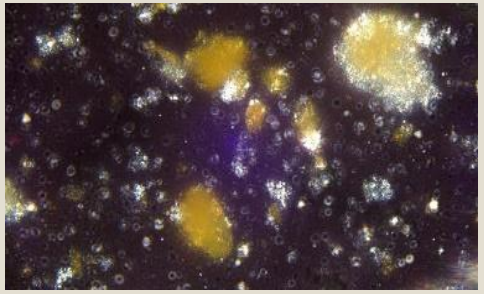
- yellow ochre

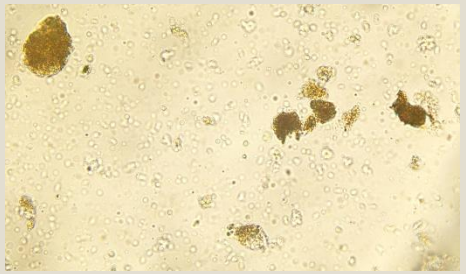
Sample cross-section

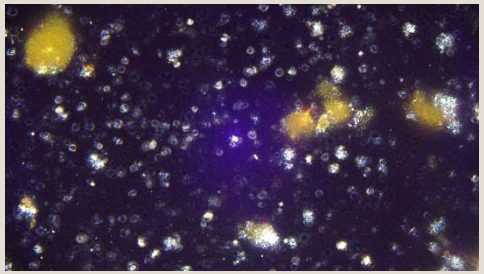


Micrographs







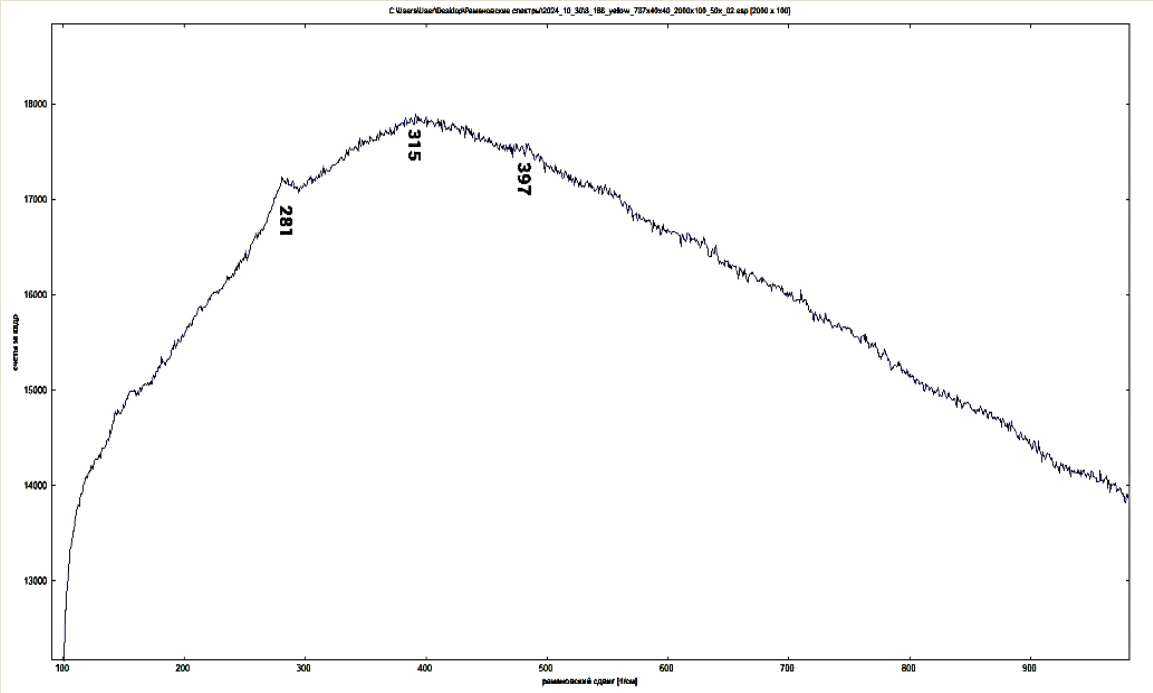


Fragment with yellow paint layer

XRF

Color (8/169)	Chemical elements
Yellow	Ca, K, Si, Fe, Al, Mn, Ti, S, P

μ-Raman



Researches

Paint layers

- X-ray fluorescence analysis (XRF)
- Raman spectroscopy
- Polarized microscopy
- Stratigraphy
- Scanning electron microscopy with hitage energy dispersive X-ray spectroscopy (SEM-EDS)

Plasters

- Neutron activation analysis (NAA)
- Statistical analysis of NAA data
  - Hierarchical cluster analysis
  - Principal component analysis
  - K-means method

Neutron activation analysis

Sample preparation:

- clearing => grinding => drying;
- 30 fragments;
- 3 subsamples of 0.1 g±0.01 g;
- SLI and LLI.

MFI Dremel

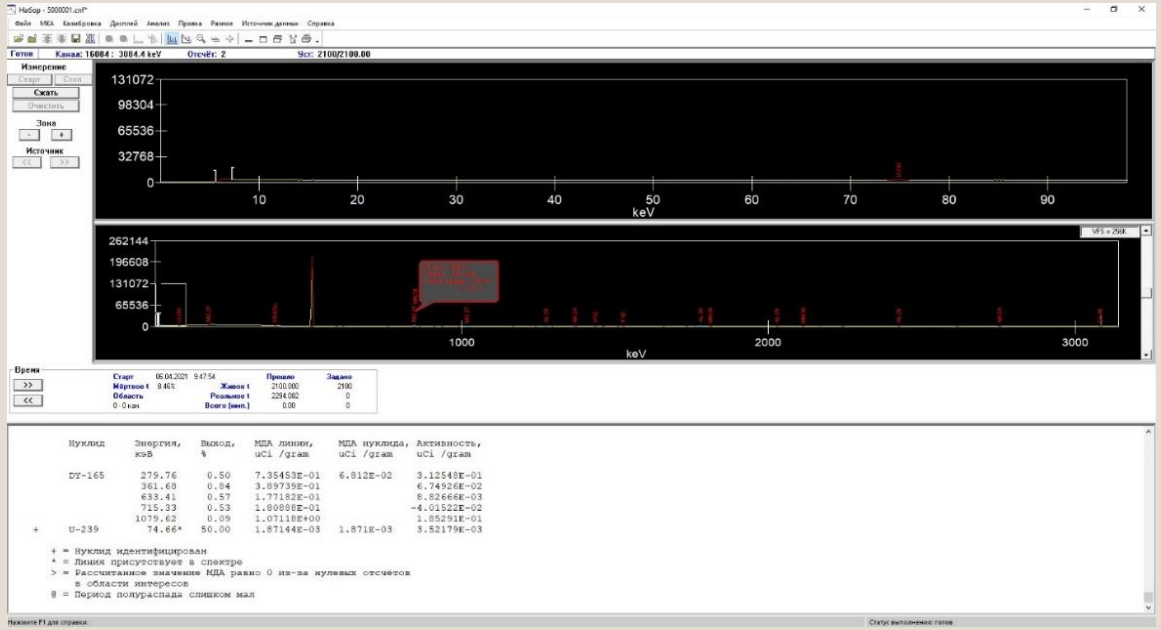
Ball Mill Fritsch

Drying cabinet

Irradiation in the Institute of Nuclear Physics (INP)

	"dry" channel	"wet" channel
Measurement type	SLI	LLI
Thermal neutron flux, n/(cm^{2}s)	4,4 x 10^{12}	6.2 x 10^{13}
Resonance neutron flux, n/(cm^{2}s)	3,8 x 10^{10}	3,0 x 10^{12}
HPGe detector	Canberra GC2018	ORTEC GEM40P44083

Spectra processing in the program Genie2000:



NAA Results

Macro-elements

Elements	Mean±Se	Median	Min-Max
Na	784.1±298.3	577.5	340 -2220
Mg	6524±629	6386	5019-8445
Al	10614±996	10036	8907-14529
K	4869±1309	4225	1810-11700
Ca	332042±11792	332042	300000 - 370000
Fe	7254 ±792	7254	5990-9600

Micro-elements

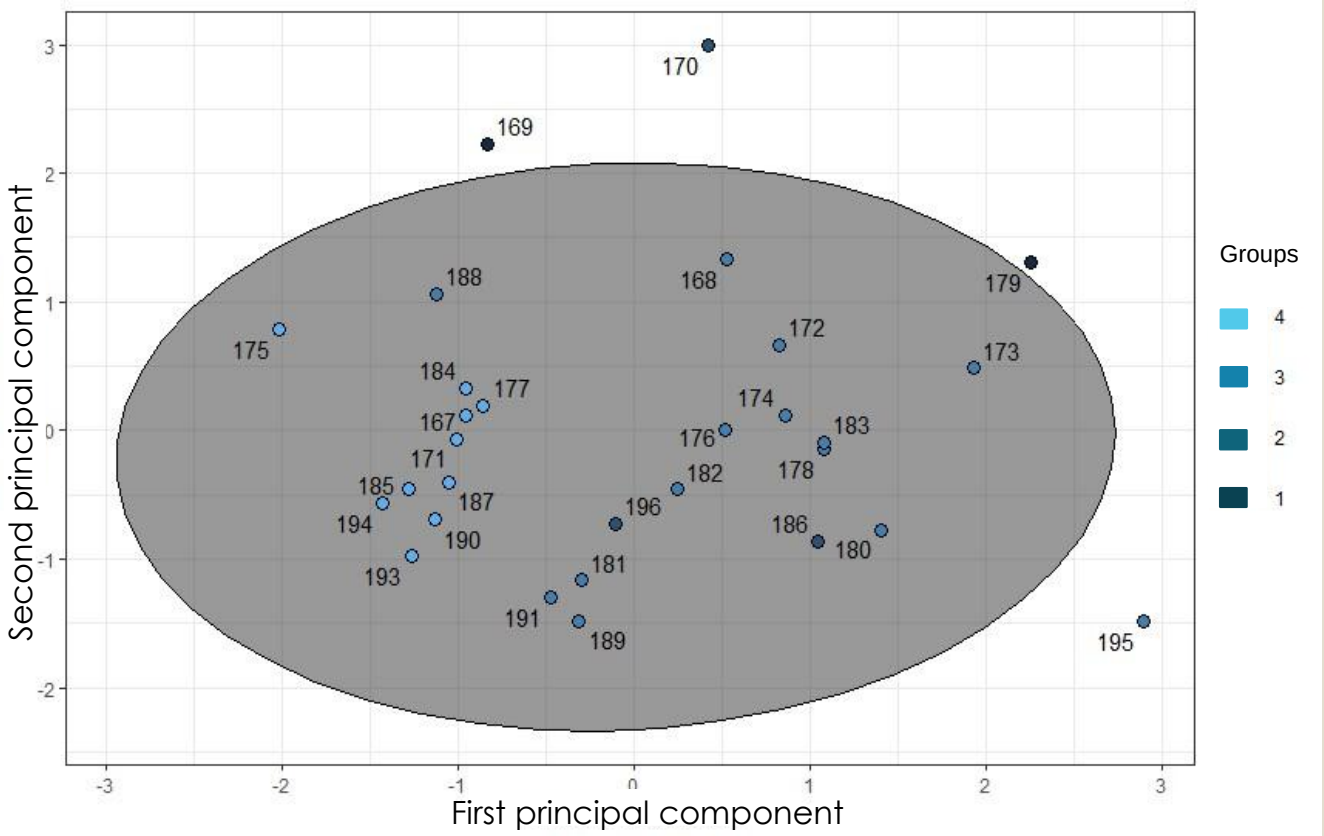
Elements	Mean±Se	Median	Min-Max
Ti	519-248	528.2	345-714
V	14.2-3.2	14.5	9.7-18.9
Cr	11.1-5.1	11.1	8.8-13.9
Mn	555-183	555.3	404-699
Co	1.9-0.4	1.9	1.3-3.9
Zn	12.1-5.4	12.1	7.7-18.4
As	1.6-0.4	1.5	1.2-2.4
Br	4.8-2.5	4.8	3.01-7.44
Sr	199-109	119.6	89.8-297.9
Zr	30.1-8.76	27.8	18.1-49.4
La	8.5-1.5	8.9	6.5-9.5

Statistical analysis

Hierarchical cluster analysis, principal component analysis, linear discriminant analysis

Attempt to perform statistical analysis using the principal component analysis

Statistical analysis didn't allow dividing plasters into separate groups. Therefore, it can be concluded that all samples dated back to the 12th century.



Comparison

The Church of Transfiguration of Our Savior on the Nereditsa Hill

The Church of St. John the Baptist on Opoki

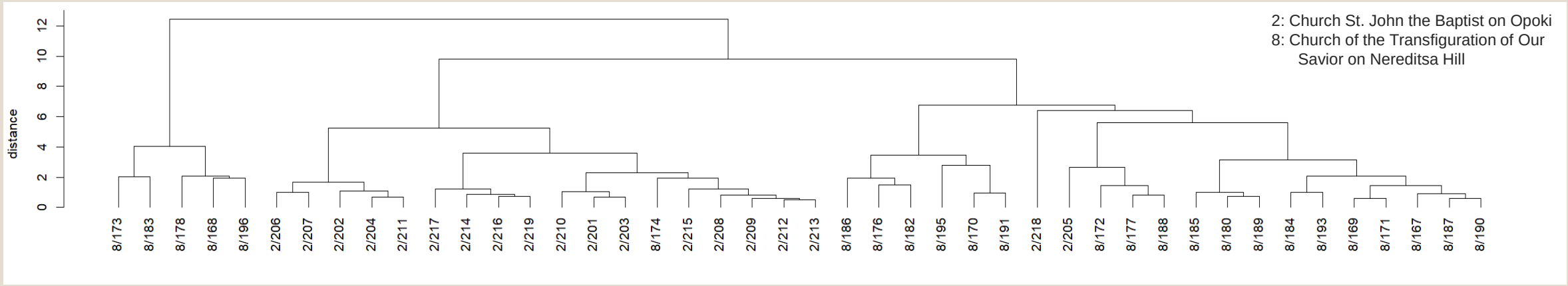
NAA results for macro-elements

Church of the Transfiguration of Our Savior on Nereditsa Hill

Elements	Mean±Se	Median	Min-Max
Na	784.1±298.3	577.5	340 -2220
Mg	6524±629	6386	5019-8445
Al	10614±996	10036	8907-14529
K	4869±1309	4225	1810-11700
Ca	332042±11792	332042	300000 - 370000
Fe	7254 ±792	7254	5990-9600

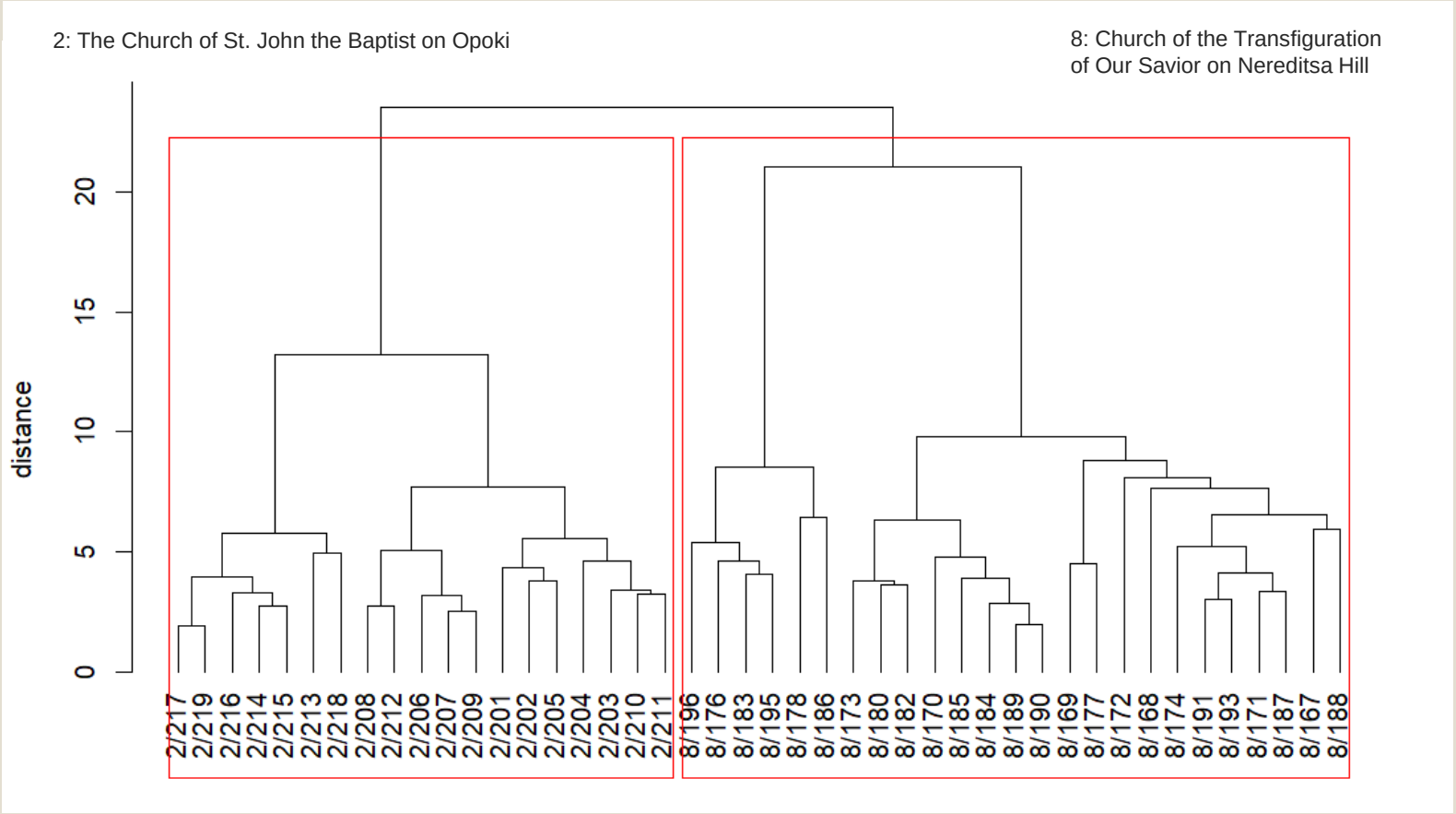
Church St. John the Baptist on Opoki

Elements	Mean±Se	Median	Min-Max
Na	603.9±151.8	585.9	348.8 -1485.6
Mg	8144 ±975	8099	6348-9797
Al	6963 ±540	6932	4792 -8616
K	1385.0 ±403.5	1397.8	768.9-2599.6
Ca	343157 ±9410	344043	323169 - 369855
Fe	6886 ±470	6751	5371-8412

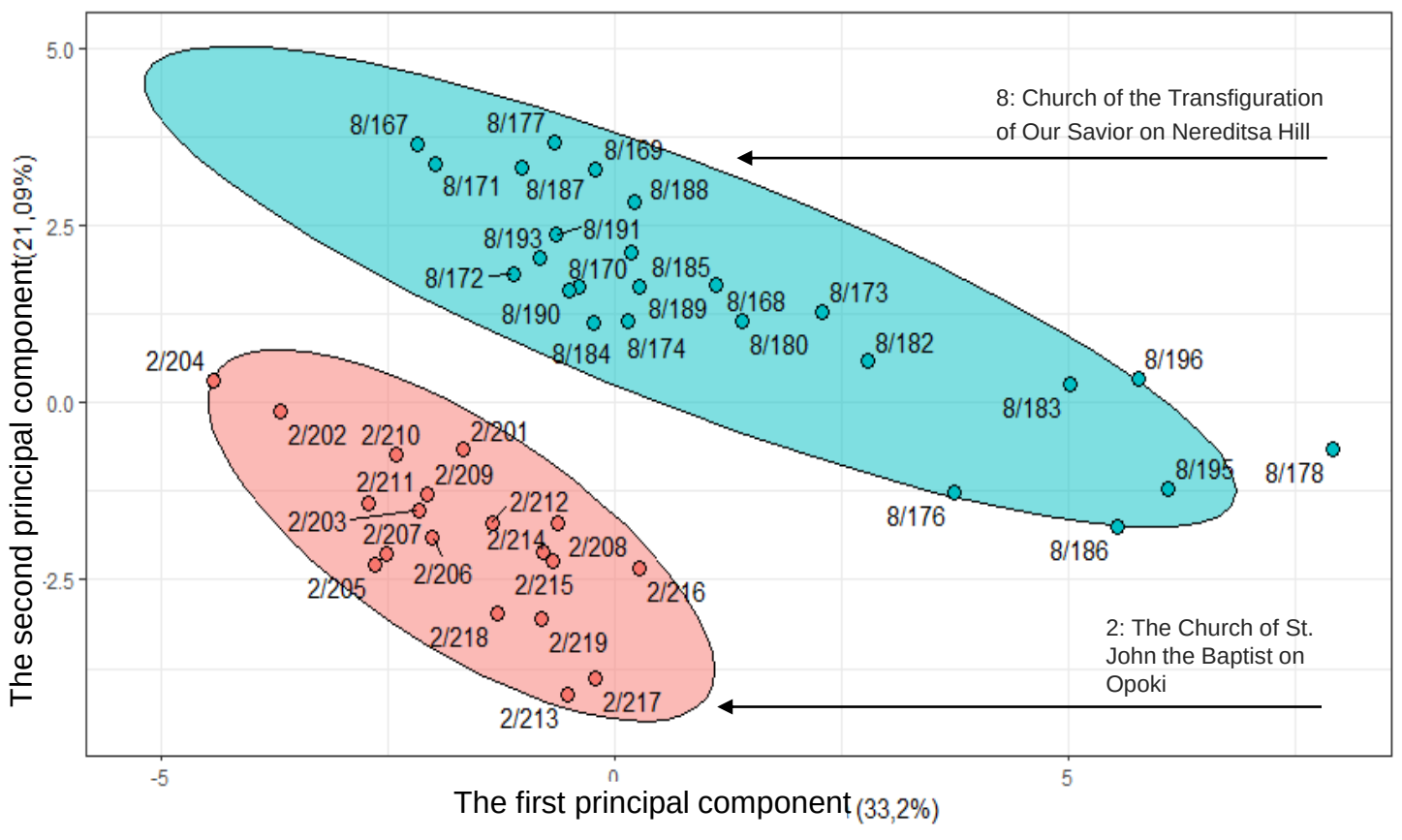


Hierarchical cluster analysis

- Separation by micro-elements
- Scale method
- Ward method
- Euclidean distance

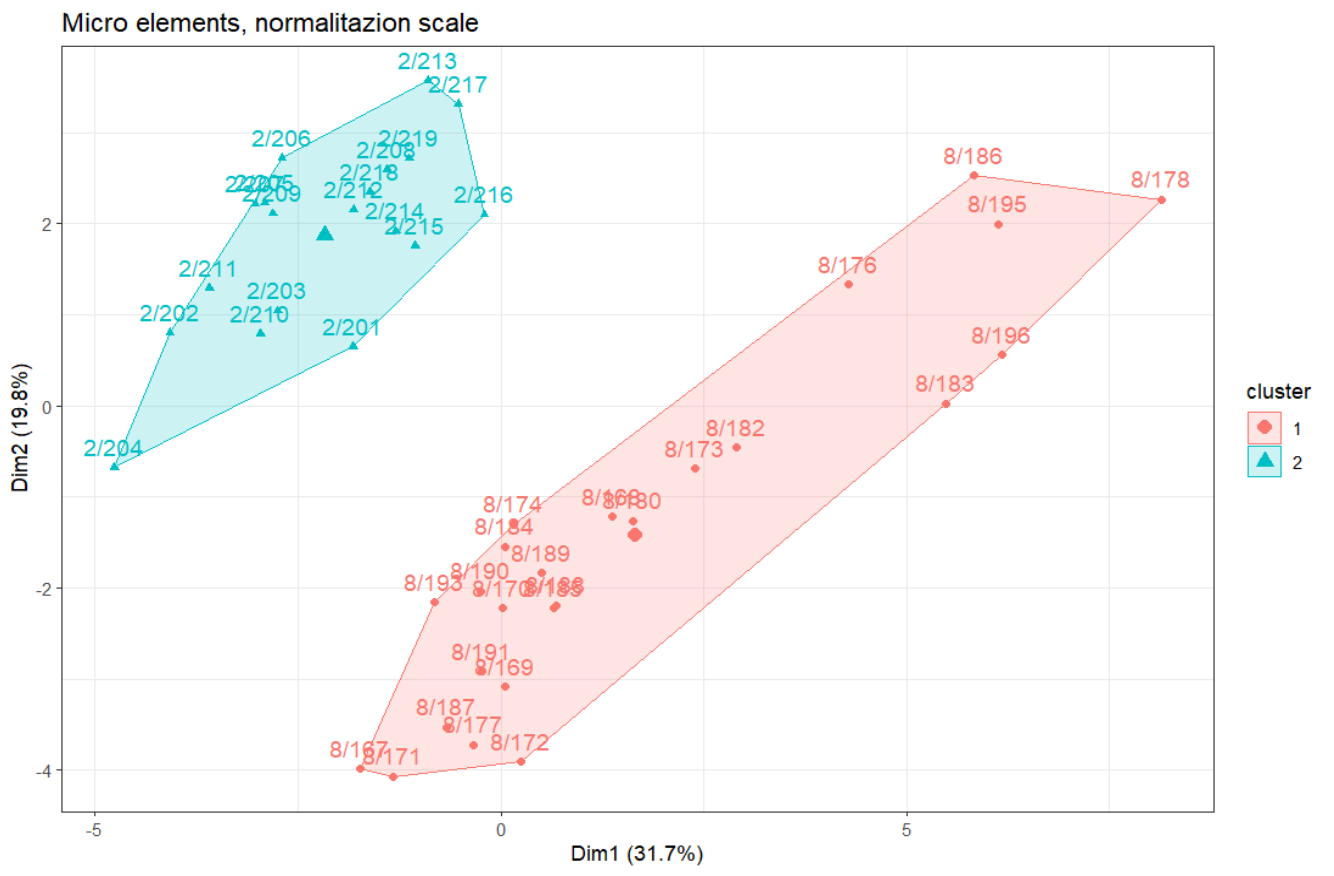


Principal component analysis



The samples were divided into two separate groups and didn't mix. The principal component analysis confirms the separation of two monuments made according to the same recipe according to the micro-element composition of the plasters.

K-means method



The samples were divided into 2 separate groups and didn't mix. K-means method confirms the separation of 2 monuments made according to the same recipe according to the micro-element composition of the plasters.

Conclusions

- A comprehensive study of fragments of wall paintings of the Church of the Transfiguration of Our Savior on the Nereditsa Hill was performed;
- A set of pigments and the structure of wall paintings were identified;
- The main pigments are red and yellow ochres, green earth, lazurite, soot and lime white. The number of color layers varies from 1 to 5;
- Statistical analysis didn't allow dividing plasters into separate groups. So we can assume all the studied fragments belong to the author's painting of the 12^{th} century;
- A statistically significant difference in the micro-element composition of the plasters of two monuments of the 12^{th} century was revealed, despite the use of the same recipes.

Thanks for your attention